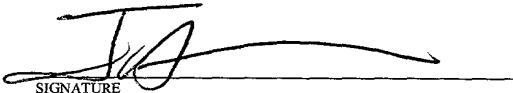


3712 Rec'd PCT/PTO 27 FEB 2009

FORM PTO-1390 TRADEMARK OFFICE (REV 9-2001)		U.S. DEPARTMENT OF COMMERCE PATENT AND	ATTORNEY'S DOCKET NUMBER
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371		TS0793 US US APPLICATION NO. (If known, see 37 CFR 1.5)	
INTERNATIONAL APPLICATION NO. PCT/EP00/08441	INTERNATIONAL FILING DATE 29 August 2000	PRIORITY DATE CLAIMED 31 August 1999	
TITLE OF INVENTION: CATALYTIC OXIDATION PROCESS WITH FLOW CONTROL SYSTEM			
APPLICANT(S) FOR DO/EO/US: KUIPERS, Herman, Pieter, Charles, Eduard and WENTINCK, Hendrik, Martinus			
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:			
<ol style="list-style-type: none"> 1. <input checked="" type="checkbox"/> This is a FIRST submission of items concerning a filing under 35 U.S.C. 371. 2. <input type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371. 3. <input type="checkbox"/> This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below. 4. <input type="checkbox"/> The US has been elected by the expiration of 19 months from the priority date (PCT Article 31). 5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2)). <ol style="list-style-type: none"> a. <input type="checkbox"/> is attached hereto (required only if not communicated by the International Bureau). b. <input checked="" type="checkbox"/> has been communicated by the International Bureau. c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US). 6. <input type="checkbox"/> An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)). <ol style="list-style-type: none"> A <input type="checkbox"/> is attached hereto b. <input type="checkbox"/> has been previously submitted under 35 U.S.C. 154(d)(4). 7. <input checked="" type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)). <ol style="list-style-type: none"> a. <input type="checkbox"/> are attached hereto (required only if not communicated by the International Bureau). b. <input type="checkbox"/> have been communicated by the International Bureau. c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired. d. <input checked="" type="checkbox"/> have not been made and will not be made. 8. <input type="checkbox"/> An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)). 9. <input checked="" type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)). 10. <input type="checkbox"/> An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)). 			
Items 11 to 16 below concern document(s) or information included:			
<ol style="list-style-type: none"> 11. <input checked="" type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98. 12. <input checked="" type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included. 13. <input checked="" type="checkbox"/> A FIRST preliminary amendment. 14. <input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment. 15. <input type="checkbox"/> A substitute specification. 16. <input type="checkbox"/> A change of power of attorney and/or address letter. 17. <input type="checkbox"/> A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821-1.825 18. <input type="checkbox"/> A second copy of the published international application under 35 U.S.C. 154(d)(4). 19. <input type="checkbox"/> A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4). 20. <input checked="" type="checkbox"/> Other items or information: postcard for date stamping only 			

JC13 Rec'd PTO/PTO 27 FEB 2002

U.S. APPLICATION NO. (If known, see 37 CFR 1.1)		INTERNATIONAL APPLICATION NO PCT/EP00/08441	ATTORNEY'S DOCKET NUMBER TS0793 US
21. <input checked="" type="checkbox"/> The following fees are submitted:		CALCULATIONS PTO USE ONLY	
Basic National Fee (37 CFR 1.492(a)(1)-(5)):			
Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO		\$104.00	
International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO		\$890.00	
International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO		\$740.00	
International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4)		\$710.00	
International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4)		\$100.00	
ENTER APPROPRIATE BASIC FEE AMOUNT =		\$890.00	
Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)).		\$	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE
Total Claims	11 - 20 =	0	x \$ 18.00 \$
Independent Claims	1 - 3 =	0	x \$ 84.00 \$
Multiple dependent claim(s) (if applicable)		+ \$280.00 \$	
TOTAL OF ABOVE CALCULATIONS =		\$	
<input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2.		\$	
		+ \$	
SUBTOTAL =		\$890.00	
Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)).		\$	
		+ \$	
TOTAL NATIONAL FEE =		\$	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property		+ \$ 40.00	
TOTAL FEES ENCLOSED =		\$	
		Amount to be refunded: charged:	\$930.00
a. <input type="checkbox"/> A check in the amount of \$_____ cover the above fees is enclosed.			
b. <input checked="" type="checkbox"/> Please charge my Deposit Account No. <u>19-1800</u> in the amount of <u>\$930.00</u> to cover the above fees. A duplicate copy of this sheet is enclosed.			
c. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. <u>19-1800</u> . A duplicate copy of this sheet is enclosed.			
NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.			
SEND ALL CORRESPONDENCE TO: Jennifer D. Adamson SHELL OIL COMPANY INTELLECTUAL PROPERTY P. O. BOX 2463 HOUSTON, TX 77252-2463 713-241-3901 713-241-6617		 SIGNATURE Jennifer D. Adamson <hr/> NAME 47,379 <hr/> REGISTRATION NUMBER	

THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re PCT International Application of)
KUIPERS, Herman, Pieter, Charles, Eduard)
and WENTINCK, Hendrik, Martinus)
Int. Appl No.: PCT/EP00/08441)
Int. Filing Date: 29 August 2000)
CATALYTIC OXIDATION PROCESS WITH)
FLOW CONTROL SYSTEM) 27 February 2002

ASSISTANT COMMISSIONER FOR PATENTS
Washington, DC 20231

PRELIMINARY AMENDMENT UNDER 37 CFR 1.115

Please enter the Article 34 Amendment before entering of the Preliminary Amendment.

IN THE ABSTRACT

Please add the following abstract:

A process for the catalytic oxidation of a hydrocarbonaceous fuel into a conversion product, wherein a feed mixture comprising the fuel and an oxygen-containing gas is contacted with a catalyst bed, comprising the steps of: (a) setting the flow rate of the fuel and flow rate of the oxygen-containing gas, (b) determining the actual temperature of the upstream surface of the catalyst bed by means of a quick response device; and (c) generating an output signal that is a function of the difference between the actual temperature and a set point for the temperature; and using the output signal to adjust the flow rate of the fuel and/or of the oxygen-containing gas.

IN THE CLAIMS

Amend claims: 1 -11.

1. (Once Amended) A process for the catalytic oxidation of a hydro-carbonaceous fuel into a conversion product, wherein a feed mixture comprising the fuel and an oxygen-containing gas is contacted with a catalyst bed, comprising:
 - (a) setting the flow rate of the fuel and the flow rate of the oxygen-containing gas;
 - (b) determining the actual temperature of the upstream surface of the catalyst bed by means of a quick response device within a time frame of from between 1 to between 100 milliseconds;
 - (c) generating an output signal that is a function of the difference between the actual temperature and a set point for the temperature; and
 - (d) using the output signal to adjust the flow rate of the fuel and/or of the oxygen-containing gas.
2. (Once Amended) The process of claim 1, wherein operating under conditions of non-steady demand of conversion product.
3. (Once Amended) The process of claim 2, wherein the turn-down ratio in demand of conversion product is in the range of from between 1:10 to between 1:100.
4. (Once Amended) The process of claim 1, wherein the set point for the temperature is determined by the value of the oxygen/carbon ratio in the feed mixture and by the demand of conversion product.
5. (Once Amended) The process of claim 1, wherein the catalytic oxidation process is a catalytic partial oxidation process and wherein the conversion product is a hydrogen-containing gas.

6. (Once Amended) The process of claim 1, wherein the quick response device comprises an optical pyrometer and wherein the determination of the actual temperature is carried out by measuring the light intensity emitted by the upstream surface of the catalyst bed.

7. (Once Amended) The process of claim 6, wherein the optical pyrometer is measuring the ratio between the light intensities emitted by the upstream surface of the catalyst bed at two different wavelength ranges.

8. (Once Amended) The process of claim 6, wherein the light intensity is measured at wavelengths in the range of from between 700 to between 1000 nm.

9. (Once Amended) The process of claim 1, wherein the adjustment of the flow rate in step (d) is carried out by means of a rapid response actuator.

10. (Once Amended) The process of claim 9, wherein the adjustment of the flow rate of the fuel is carried out by means of a pulsed liquid injection system.

11. (Once Amended) Transport means comprising a system for the catalytic partial oxidation of a fuel that is operated by the process of claim 10.

Respectfully submitted,

KUIPERS, Herman, Pieter, Charles, Eduard
and WENTINCK, Hendrik, Martinus

By: 
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MARKED UP VERSION OF AMENDED CLAIMS

1. (Amended) A process for the catalytic oxidation of a hydro-carbonaceous fuel into a conversion product, wherein a feed mixture comprising the fuel and an oxygen-containing gas is contacted with a catalyst bed, [which process comprises the steps of] comprising:

- (e) setting the flow rate of the fuel and the flow rate of the oxygen-containing gas[, preferably in accordance with the demand of conversion product and a pre-determined value of the oxygen/carbon ratio in the feed mixture];
- (f) determining the actual temperature of the upstream surface of the catalyst bed by means of a quick response device within a time frame of from between 1 to between 100 milliseconds;
- (g) generating an output signal that is a function of the difference between the actual temperature and a set point for the temperature; and
- (h) using the output signal to adjust the flow rate of the fuel and/or of the oxygen-containing gas[, preferably the flow rate of the fuel].

2. (Amended) The [A] process [according to] of claim 1, wherein operating under conditions of non-steady demand of conversion product.

3. (Amended) The [A] process [according to] of claim 2, wherein the turn-down ratio in demand of conversion product is in the range of from between 1:10 to between 1:100[, preferably of from 1:30 to 1:80].

4. (Amended) The [A] process [according to any] of claim[s] 1[to 3], wherein the set point for the temperature is determined by the value of the oxygen/carbon ratio in the feed mixture and by the demand of conversion product.

5. (Amended) The [A] process [according to any of the preceding claims] of claim 1, wherein the catalytic oxidation process is a catalytic partial oxidation process and wherein the conversion product is a hydrogen-containing gas.

6. (Amended) The [A] process [according to any of the preceding claims] of claim
1, wherein the quick response device comprises an optical pyrometer and wherein the
determination of the actual temperature is carried out by measuring the light intensity
emitted by the upstream surface of the catalyst bed.
7. (Amended) The [A] process [according to] of claim 6, wherein the optical
pyrometer is measuring the ratio between the light intensities emitted by the upstream
surface of the catalyst bed at two different wavelength ranges.
8. (Amended) The [A] process [according to] of claim 6[or 7], wherein the light
intensity is measured at wavelengths in the range of from between 700 to between 1000 nm.
9. (Amended) The [A] process [according to any of the preceding claims] of claim
1, wherein the adjustment of the flow rate in step (d) is carried out by means of a rapid
response actuator.
10. (Amended) The [A] process [according to] of claim 9, wherein the adjustment of
the flow rate of the fuel is carried out by means of a pulsed liquid injection system.
11. (Amended) Transport means comprising a system for the catalytic partial
oxidation of a fuel that is operated by the process of claim 10 [according to any of the
preceding claims].

CATALYTIC OXIDATION PROCESS WITH FLOW CONTROL SYSTEM

The present invention relates to a process for the catalytic oxidation of a hydrocarbonaceous fuel and to transport means comprising a system for the catalytic partial oxidation of a fuel that is operated according to such a process.

Catalytic oxidation processes such as catalytic partial oxidation processes, wherein a feed mixture comprising a hydrocarbonaceous fuel and an oxygen-containing gas are contacted with a catalyst are known in the art. The partial oxidation of a hydrocarbonaceous fuel, in particular hydrocarbons, in the presence of a catalyst is an attractive route for the preparation of mixtures of carbon monoxide and hydrogen. It is an exothermic reaction represented by the equation:



There is literature in abundance on the catalysts and the process for the catalytic partial oxidation of hydrocarbons. Reference is made, for instance, to US ,149,464, EP 576 096, EP 629 578, and WO 99/19249.

Such catalytic oxidation processes are susceptible to changes in the oxygen/carbon ratio in the feed mixture which has a direct influence on the reaction temperature. Since even a slight deviation from the desired ratio may shorten the life of the oxidation catalyst employed, there is a need to be able to measure the oxygen/carbon ratio or the flow rates of the oxygen-containing gas and the fuel accurately. In processes which operate under conditions which include changes, in particular frequent changes in the demand of the conversion product, and thus in throughput of the reactants, there is also a need to

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measure the oxygen/carbon ratio or the flow rates of the reactants very quickly. For instance, in the case of catalytic partial oxidation processes which are directed at producing hydrogen which is to be used as feedstock for a fuel cell as envisaged in hydrogen-operated motor cars, there will be a need for rapid and sometimes frequent decreases and increases in the flow of hydrogen to the fuel cell depending on the requirements of the motorist. Accordingly, the flow rates of fuel and oxygen-containing gas to the partial oxidation catalyst have to change rapidly and deviations from the desired oxygen/carbon ratio have to be corrected quick and accurately.

Flow metres that are able to measure the actual flow rate at the required time scale, i.e. typically in the order of 1 to 100 milliseconds, are not available or extremely expensive.

Since the oxygen/carbon ratio of the feed mixture strongly influences the reaction temperature, it is possible to monitor the oxygen/carbon ratio by monitoring the reaction temperature.

Reaction temperatures can be measured and monitored by various methods known in the art. Thermocouples are well known for temperature measurement, also at relatively high temperatures. They are reliable and normally have a long service life.

In US 5,939,025 for example, the use of thermocouples to record changes in temperature in a catalytic partial oxidation reformer due to a step change in reactant flow is described.

However, due to their relatively slow response time, thermocouples are not adequate in systems wherein rapid changes occur. Since they cannot cope with the rapid changes, their use would lead to incorrect information and improper adjustments of the oxygen/carbon ratio.

Thus, there is a need for means that can quickly and reliably monitor the actual oxygen/carbon ratio in a catalytic oxidation process wherein the flow rates of the reactants are rapidly varied.

It has now been found that quick and reliable information about the actual oxygen/carbon ratio in the feed mixture can be obtained when use is made of the colour of or light intensity emitted by the upstream surface of the catalyst bed wherein catalytic oxidation is carried out.

The present invention therefore relates to a process for the catalytic oxidation of a hydrocarbonaceous fuel into a conversion product, wherein a feed mixture comprising the fuel and an oxygen-containing gas is contacted with a catalyst bed, which process further comprises the steps of:

- (a) setting the flow rate of the fuel and the flow rate of the oxygen-containing gas, preferably in accordance with the demand of conversion product and a pre-determined value of the oxygen/carbon ratio in the feed mixture;
- (b) determining the actual temperature of the upstream surface of the catalyst bed by means of a quick response device;
- (c) generating an output signal that is a function of the difference between the actual temperature and a set point for the temperature; and
- (d) using the output signal to adjust the flow rate of the fuel and/or of the oxygen-containing gas, preferably the flow rate of the fuel.

The process according to the present invention can suitably be applied under conditions of non-steady demand of conversion product, i.e. conditions wherein the amount of conversion product produced per unit of time has to vary and therewith the flow rates of the reactants. Even

under process conditions requiring a turn-down ratio in demand of conversion product of up to 1:100, i.e. the maximum demand is a factor 100 higher than the minimum demand, the process of the present invention is particularly suitable in order to control the oxygen/carbon ratio in the feed mixture. Preferably, the turn-down ratio is in the range of from 1:10 to 1:100, more preferably in the range of from 1:30 to 1:80.

The process according to the invention will now be illustrated with reference to Figures 1 and 2.

Figure 1 schematically shows a first embodiment of the adjustment of the flow rates in a catalytic partial oxidation process according to the invention.

Figure 2 schematically shows a second embodiment of the adjustment of the flow rates in a catalytic partial oxidation process according to the invention.

A hydrocarbonaceous fuel passes through line 1 and an oxygen-containing gas passes through line 2 and are mixed before contacting the catalyst bed 3. Both the flow rate of the hydrocarbonaceous fuel and of the oxygen-containing gas are set in accordance with the hydrogen demand and a pre-determined value of the oxygen-carbon ratio in the feed by adjusting means 4 and 5, respectively. Thereto, input signals 6 and 7, which are each determined by the hydrogen demand and the pre-determined value of the oxygen-carbon ratio, are fed to the adjusting means 4 and 5, respectively.

The amount of fuel needed per unit of time, and thus the desired flow rate of the fuel, largely depends on the hydrogen demand. It will be appreciated that the flow rate of the fuel and the flow rate of the oxygen-containing gas are correlated via the desired oxygen/carbon ratio in the feed, i.e. the pre-determined value of the oxygen/carbon ratio.

In a catalytic partial oxidation process, the desired oxygen/carbon ratio will be substantially constant over a wide range of hydrogen demand. It will be appreciated, however, that the desired oxygen/carbon ratio is to some extent dependent of the hydrogen demand. For example, at low hydrogen demand, and thus low throughput of the reactants, heat losses are relatively high and it may be desired to produce extra heat by using a higher oxygen/carbon ratio in the feed mixture. The skilled person is familiar with such effects.

The setting of the flow rates in accordance with the hydrogen demand and the pre-determined value of the oxygen/carbon ratio may however lead to slight deviations of the actual oxygen/carbon ratio from the pre-determined value of the oxygen/carbon ratio. In order to correct such deviations, the actual temperature of the upstream surface 8 of the catalyst bed 3 is determined by means of a quick response device 9.

A signal 10 representing the actual temperature as determined by device 9 and a signal 11 representing a set point for the temperature are fed to control unit 12 and an output signal 13 is generated as a function of the difference between the actual temperature and the set point for the temperature. The output signal 13 is fed to adjusting means 4 in order to adjust the flow rate of the fuel. Control unit 12 may be any data processor capable of receiving signals within the time frame applicable in determining the temperature of the upstream surface of the catalyst bed.

In the embodiment of the process shown in Figure 1, the output signal 13 is used to adjust the flow rate of the fuel. Alternatively, the output signal may be used to adjust the flow rate of the oxygen-containing gas or of both the fuel and the oxygen-containing gas.

5 Signals 6 and 13 may be fed to the same adjusting means in order to set and adjust the flow rate of the fuel, such as shown in Figure 1. Alternatively, signals 6 and 13 may be fed to different adjusting means in line 1 in order to set and adjust the flow rate of the fuel, respectively.

10 In the embodiment of the process shown in Figure 1, the fuel flow rate is adjusted by means of feedback control, i.e. the output signal 13 is directly used to adjust the fuel flow rate. The flow rate is thus adjusted in reaction on the actual temperature of the upstream surface of the catalyst as determined by quick response device 9.

15 Preferably, the flow rate of the fuel or the oxygen-containing gas is adjusted by means of a combined feedforward and feedback control, such as illustrated in Figure 2. In this so-called pro-active feedback mode, information on temperature deviations during a transient is used to pro-actively adjust the flow rate during a later transient. Thereto, output signal 13 is fed to feedforward control unit 14. In feedforward control unit 14, output signal 15 is generated using the input signals 6 and 7, and the information contained in output signal 13 generated during an earlier, similar transient. Output signal 15 is directly fed to adjusting means 4 to 20 adjust the flow rate of the fuel.

25 The adjusting means may be any means known in the art, for example an adjustable valve, injector or vaporiser, or a flow restriction. Preferably, the adjustment of the flow rate of the fuel and/or the oxygen-containing gas is carried out by means of a rapid response actuator. In a particularly preferred embodiment of the process according to the invention, the fuel flow rate is set and adjusted by adding the required amount of 30 fuel to the stream of oxygen-containing gas flowing in

line 2 by means of a pulsed liquid injector. Suitable pulsed liquid injection systems are known in the art and commercially available, for example from Bosch and Mitsubishi.

Such system is operated by setting the frequency and the width of the pulse. It is triggered by input signal 6 and output signal 13 or 15 and is capable of reacting quickly on those signals. It has been found that deviations from the desired oxygen/carbon ratio become smaller, and, hence, the performance in adjusting the fuel flow rate more sophisticated, when use is made of pulses having a smaller width and/or when the dead period between subsequent pulses is minimised. It has been found that the use of pulsed injection systems allows control of the oxygen/carbon ratio at high precision for turn down ratios in hydrogen demand of up to 1:100. Moreover, such systems are capable of maintaining adequate droplet size distribution even when atomisation is carried out under low flow rate conditions. The use of short, strong injections compensates for the lack of turbulence at relatively low fuel flow rates. Such pulsed liquid injection systems normally include a mixing chamber, in which the liquid is injected into another stream. The volume of the mixing chamber is suitable such that the residence time of the liquid is several times the dead period between the pulses.

In the process according to the present invention, the temperature of the upstream surface of the catalyst bed is determined, since at this location, the temperature is, for a given throughput of fuel, closely related to the oxygen/carbon ratio in the feed mixture. Due to the fact that catalytic oxidation reactions proceed at very short contact times, the oxidation reactions mainly takes place in the upstream layer of the catalyst bed and the temperature in that layer reflects

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the stoichiometry of that reaction as expressed by the oxygen/carbon ratio and also reflects changes in that ratio. At more downstream locations in the bed, these changes in temperature are damped due to the thermal mass of the catalyst and can thus not be monitored.

10 The temperature of the upstream surface is determined by means of a quick response device in order to be able to monitor rapid changes in temperature. Preferably, the temperature determination is carried out within a time frame of up to 100 milliseconds, more preferably of from 1 to 100 milliseconds, even more preferably of from 5 to 30 milliseconds.

15 It is important that the quick response device does not disturb the actual temperature of the upstream surface of the catalyst bed and that it determines the temperature of the surface and not that of the gas phase. For that reason, and apart from the fact that they have a slow response, thermocouples are not suitable to be used in the process of the present invention for determination of the upstream surface temperature. A thermocouple will disturb the surface temperature and the measured temperature will typically reflect a temperature that lies between the temperature of the gas phase and that of the surface.

20 25 A suitable means for quick and reliable determination of the temperature of the upstream surface comprises a photo detecting device, such as an optical pyrometer. Such apparatus operates on the basis of measuring the colour of or light intensity emitted by a surface using an optical fibre. The light intensities measured are converted via amplifiers and A-D current converters into a signal which can be processed in a control unit. Pyrometers are suitably made of glass or quartz, e.g. in the form of a glass rod or a glass fibre and may contain

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a silicon chip or other recording device capable of receiving and transmitting data.

During normal operation of a catalytic partial oxidation process, the upstream surface of the catalyst bed is glowing and changes in the oxygen/carbon ratio will influence the intensity and the wavelength of the light emitted by the glowing catalyst surface. The time involved in determining the temperature using a pyrometer is in the order of 1-100 milliseconds, preferably in the range between 5 and 30 milliseconds. This is sufficient to allow a quick measurement to start adjustment of the flow rate, if necessary.

Best results will be obtained when, instead of the absolute light intensity, the ratio between the light intensities emitted in different wavelength ranges is measured, preferably in two different wavelength ranges. This type of measurement is advantageous in that it reduces or even eliminates unwanted influences such as the position of reactor parts near the upstream surface, e.g. a diaphragm when used to shield part of the surface of the catalyst, or the presence of some local "dead spots" on the catalyst surface or the occurrence of achromatic fouling. Dual-wavelength pyrometers are commercially available from a number of companies and can be operated within the temperature ranges and wavelengths envisaged for the process according to the present invention.

It has been found that good results can be obtained when the colour or light intensity measurements are carried out using a pyrometer operable in the wavelength range of from 700 to 1000 nm (near infrared), as this is the range of highest sensitivity for changes in colour for silicon-type photo-detection. Preference is given to measurements performed in the 700 to 950 nm range.

Calibration of the optical pyrometer, i.e. recording the relationship between light intensity or colour and temperature may be carried out before the pyrometer is used in the present process. Calibration and re-calibration may also be carried out during operation of the present process during periods wherein the process conditions are stationary or quasi stationary, by measuring the temperature downstream of or in the downstream part of the catalyst bed. Reference herein to stationary or quasi-stationary conditions is to conditions during which the temperature variations of the catalyst bed are less than 20 °C/minute. For instance, when a vehicle is operated in a constant mode, i.e. demanding the same amount of electricity, and hence, hydrogen, over a period of time which is at least longer than the slowest response time, calibration can be carried out conveniently. For calibration purposes, a conventional temperature measurement device, such as a thermocouple, may be used to measure the downstream temperature. In practice, one will observe an offset in temperature between the upstream layer of the catalyst bed and the downstream part thereof. The magnitude of the offset will depend inter alia on the occurrence of different reactions, such as water-gas shift reactions or endothermic reforming reactions, in the downstream part of the catalyst bed and on the construction of the catalytic system applied. This does not play a major role in the proper calibration of the quick response device. Those skilled in the art will be familiar with such effects.

It will be clear that during start-up of the process of the invention, the upstream surface of the catalyst bed does not (yet) glow and is therefore not capable of emitting light having the wavelengths on which the

monitoring system is based. Therefore, at start-up, an estimate of the flow rates of fuel and oxygen-containing gas needed to cause the catalyst bed to start glowing will be made. At a certain signal/noise ratio adjustment of the flow rate according to the invention will be carried out.

The process according to the invention may be operated by setting the set point for the temperature independently from the hydrogen demand and the desired oxygen/carbon ratio. Preferably, however, the set point for the temperature is determined by the hydrogen demand and the predetermined oxygen/carbon ratio. It will be appreciated that the predetermined oxygen/carbon ratio may to some extent depend on the hydrogen demand.

It will be appreciated that the dependency of the temperature of the upstream surface on the hydrogen demand and oxygen/carbon ratio can change, for example due to degradation of the catalyst. Such changes may be taken into account by adjusting the set point for the temperature. Data for the required adjustment may be obtained by measuring process features, for example temperature or pressure, occurring downstream of the catalyst bed during periods of stationary or quasi stationary process conditions, i.e. wherein the flow rates and the oxygen/carbon ratio are substantially constant.

The process according to the invention is not only particularly suitable for controlling the oxygen/carbon ratio in catalytic oxidation processes wherein the demand of conversion products, and thus the fuel flow rate, is varying, but also for controlling the oxygen/carbon ratio in catalytic oxidation processes wherein the fuel composition, and thus the carbon content, is varying. This is for instance the case when using off-shore gas as fuel.

The catalytic oxidation process according to the invention is preferably a catalytic partial oxidation process. Catalytic partial oxidation processes are typically carried out by contacting a feed mixture comprising a hydrocarbonaceous feedstock and an oxygen-containing gas with a suitable catalyst, preferably in amounts giving an oxygen/carbon ratio in the range of from 0.3 to 0.8, more preferably of from 0.45 to 0.75, even more preferably of from 0.45 to 0.65. References herein to oxygen/carbon ratio are to the ratio of oxygen in the form of molecules O₂ to carbon present in the fuel.

The feed mixture may comprise steam and/or carbon dioxide. If steam is present in the feed mixture, the steam/carbon ratio, i.e. the ratio of molecules of steam (H₂O) to carbon in the fuel, is preferably in the range of from above 0.0 to 3.0, more preferably of from above 0.0 to 2.0.

The hydrocarbonaceous fuel may comprise hydrocarbons and/or oxygenates which are gaseous at the temperature and pressure prevailing in the catalyst bed during normal operation of the catalytic partial oxidation process. Particular suitable fuels comprise hydrocarbons which are gaseous or liquid under standard conditions of temperature and pressure (STP, i.e. at 0 °C and 1 atmosphere), such as natural gas, naphtha, kerosene, or gas oil. Reference herein to oxygenates is to molecules containing, apart from carbon and hydrogen atoms, at least one oxygen atom which is linked to either one or two carbon atoms or to a carbon atom and a hydrogen atom, such as alcohols, ethers, acids and esters.

Reference herein to an oxygen-containing gas is to a gas containing molecular oxygen, for example air,

substantially pure oxygen or oxygen-enriched air. The oxygen-containing gas preferably is air.

The temperature prevailing in a catalytic partial oxidation process is typically in the range of from 750 to 1500 °C, preferably of from 800 to 1350 °C, more preferably of from 850 to 1300 °C. Reference herein to temperature is to the temperature in the upstream layer of the catalyst bed.

The catalytic partial oxidation process is typically operated at a pressure in the range of from 1 to 100 bar (absolute), preferably in the range of from 1 to 50 bar (absolute), more preferably of from 1 to 10 bar (absolute).

In the catalytic partial oxidation process in accordance with the present invention, the throughput of feed mixture and thus the gas hourly space velocity, expressed as normal litres of gas per kilogram of catalyst per hour, can be varied, depending on the hydrogen demand as triggered by the electricity needed by the motorist. At maximum feed throughput, the feed mixture is preferably contacted with the catalyst bed at gas hourly space velocities which are in the range of from 20,000 to 10,000,000 Nl/kg/h, more preferably in the range from 50,000 to 5,000,000 Nl/kg/h, even more preferably in the range of from 100,000 to 3,000,000 Nl/kg/h. Reference herein to normal litres is to litres at STP.

Catalyst compositions suitable for use in catalytic partial oxidation are known in the art. Such catalysts generally comprise, as catalytically active component, a metal selected from Group VIII of the Periodic Table of the Elements. Catalysts comprising, as the catalytically active component, a metal selected from rhodium, iridium,

palladium and platinum are preferred. Catalysts comprising rhodium and/or iridium are most preferred.

The catalytically active metal is most suitably supported on a carrier, such as refractory oxide particles, monolith structures, or metallic arrangements such as metal gauzes or arrangements of metal wires. Suitable carrier materials are well known in the art and include refractory oxides, such as silica, alumina, titania, zirconia and mixtures thereof, and aluminium-containing high-temperature resistant alloys.

Typically, the catalyst comprises the active metal in an amount in the range of from 0.01 to 20% by weight, based on the weight of carrier material, preferably from 0.02 to 10% by weight, more preferably from 0.1 to 7.5% by weight.

The catalytic partial oxidation process according to the present invention is suitably used to prepare hydrogen or a mixture of hydrogen and other gases from any hydrocarbonaceous feedstock. Preferably, the process according to the present invention is directed at producing hydrogen from fuel, in particular at the on-board production of hydrogen in fuel cell powered transport means, such as automotive vehicles and crafts.

Accordingly, the present invention also relates to transport means comprising a system for the catalytic partial oxidation that is operated as hereinabove defined.

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1. A process for the catalytic oxidation of a hydro-carbonaceous fuel into a conversion product, wherein a feed mixture comprising the fuel and an oxygen-containing gas is contacted with a catalyst bed, which process further comprises the steps of:

5 (a) setting the flow rate of the fuel and the flow rate of the oxygen-containing gas, preferably in accordance with the demand of conversion product and a pre-determined value of the oxygen/carbon ratio in the feed mixture;

10 (b) determining the actual temperature of the upstream surface of the catalyst bed by means of a quick response device within a time frame of from 1 to 100 milliseconds;

(c) generating an output signal that is a function of the difference between the actual temperature and a set point for the temperature; and

15 (d) using the output signal to adjust the flow rate of the fuel and/or of the oxygen-containing gas, preferably the flow rate of the fuel.

20 2. A process according to claim 1 operating under conditions of non-steady demand of conversion product.

3. A process according to claim 2, wherein the turn-down ratio in demand of conversion product is in the range of from 1:10 to 1:100, preferably of from 1:30 to 1:80.

25 4. A process according to any of claims 1 to 3, wherein the set point for the temperature is determined by the value of the oxygen/carbon ratio in the feed mixture and by the demand of conversion product.

5. A process according to any of the preceding claims, wherein the catalytic oxidation process is a catalytic

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partial oxidation process and wherein the conversion product is a hydrogen-containing gas.

6. A process according to any of the preceding claims, wherein the quick response device comprises an optical pyrometer and wherein the determination of the actual temperature is carried out by measuring the light intensity emitted by the upstream surface of the catalyst bed.

10 7. A process according to claim 6, wherein the optical pyrometer is measuring the ratio between the light intensities emitted by the upstream surface of the catalyst bed at two different wavelength ranges.

15 8. A process according to claim 6 or 7, wherein the light intensity is measured at wavelengths in the range of from 700 to 1000 nm.

9. A process according to any of the preceding claims, wherein the adjustment of the flow rate in step (d) is carried out by means of a rapid response actuator.

20 10. A process according to claim 9, wherein the adjustment of the flow rate of the fuel is carried out by means of a pulsed liquid injection system.

11. Transport means comprising a system for the catalytic partial oxidation of a fuel that is operated according to any of the preceding claims.

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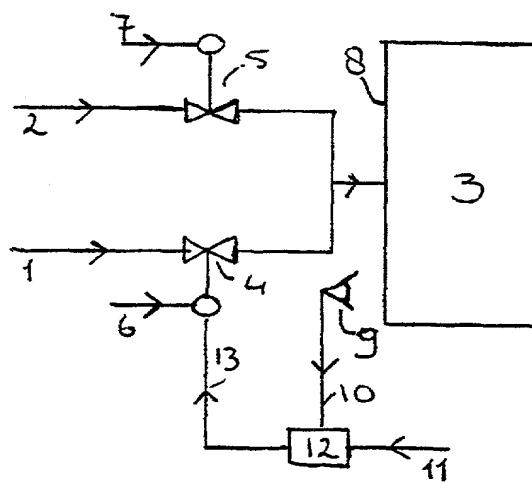
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(54) Title: CATALYTIC OXIDATION PROCESS WITH FLOW CONTROL SYSTEM



(57) Abstract: A process for the catalytic oxidation of a hydrocarbonaceous fuel (1) into a conversion product, wherein a feed mixture comprising the fuel and an oxygen-containing gas (2) is contacted with a catalyst bed (3), which process further comprises the steps of: (a) setting the flow rate of the fuel and flow rate of the oxygen-containing gas, preferably in accordance with the demand of conversion product and a pre-determined value of the oxygen/carbon ratio in the feed mixture; (b) determining the actual temperature (10) of the upstream surface of the catalyst bed by means of a quick response device; (c) generating an output signal (13) that is a function of the difference between the actual temperature and a set point for the temperature; and (d) using the output signal to adjust the flow rate of the fuel (6) and/or of the oxygen-containing (7) gas, preferably the flow rate of the fuel.

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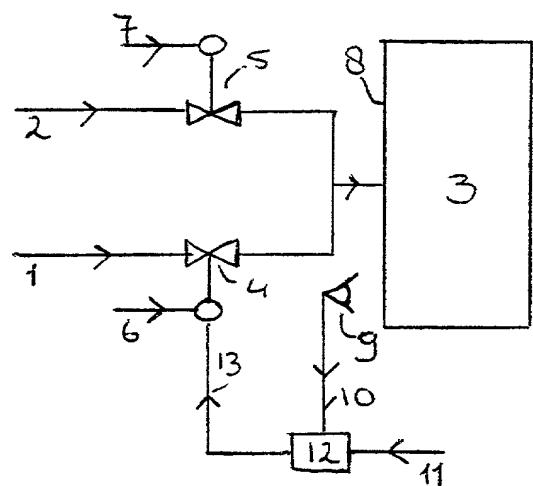


Fig 1

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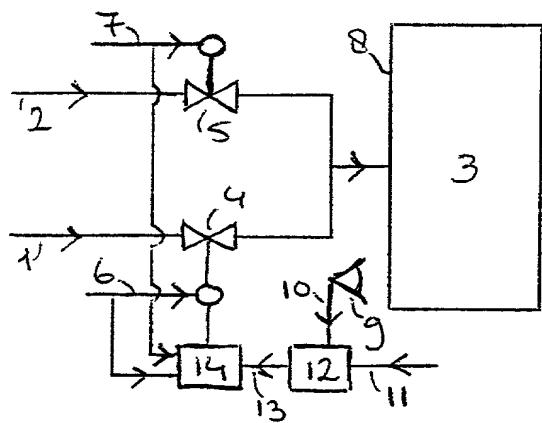


Fig 2

DECLARATION AND POWER OF ATTORNEY FOR PATENT APPLICATION

As a below named inventor, I hereby declare that:

My residence, post office address, and citizenship are as stated below next to my name. I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

Catalytic oxidation process with flow control system

the specification of which is attached hereto

unless the following box is checked:

was filed on 29 August 2000 as United States Application Number or PCT International Application Number PCT/EP00/08441 and was amended on 12-10-2001 (if applicable).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR § 1.56.

I hereby claim foreign priority benefits under 35 U.S.C. § 119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed.

PRIOR FOREIGN APPLICATION(S)

Priority
Not Claimed

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<u>99306900.4</u>	<u>EP</u>	<u>31 August 1999</u>	<input type="checkbox"/>
APPLICATION NUMBER	COUNTRY	DAY/MONTH/YEAR FILED	<input type="checkbox"/>

I hereby claim the benefit under 35 U.S.C. § 119(e) of any United States provisional application(s) listed below.

APPLICATION SERIAL NO.	FILING DATE
<u> </u>	<u> </u>

I hereby claim the benefit under 35 U.S.C. § 120 of any United States application(s) or § 365(c) of any PCT International application designating the United States, listed below and insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. § 112, I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR § 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.

APPLICATION SERIAL NO.	FILING DATE	STATUS-PATENTED, PENDING, ABANDONED
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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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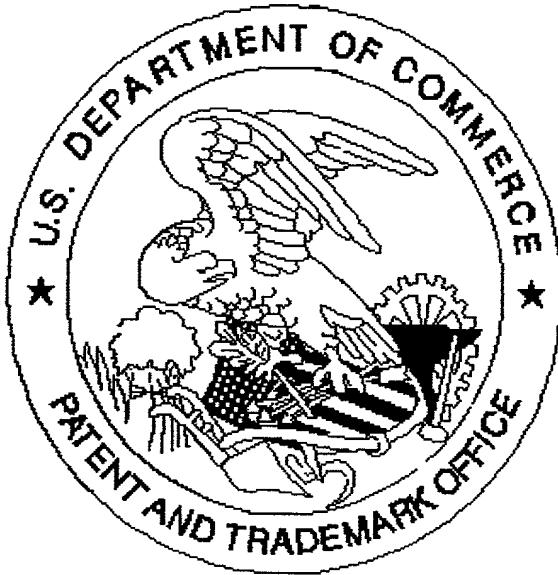
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